

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
30 June 2005 (30.06.2005)

PCT

(10) International Publication Number
WO 2005/060008 A1

(51) International Patent Classification⁷: **H01L 31/0224**,
31/042

2600 (AU). EVANS, Graeme, Leslie [AU/AU]; 8 Karney
St, Kambah, ACT 2902 (AU).

(21) International Application Number:
PCT/AU2004/001768

(74) Common Representative: **SKRYABIN, Igor**; Smart
Technologies, PO Box 6212, Queanbeyan, NSW 2620
(AU).

(22) International Filing Date:
17 December 2004 (17.12.2004)

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2003906985 18 December 2003 (18.12.2003) AU

(71) Applicant (*for all designated States except US*): **SMART
TECHNOLOGIES AUSTRALIA PTY LTD** [AU/AU];
11 Aurora Ave, Queanbeyan, NSW 2620 (AU).

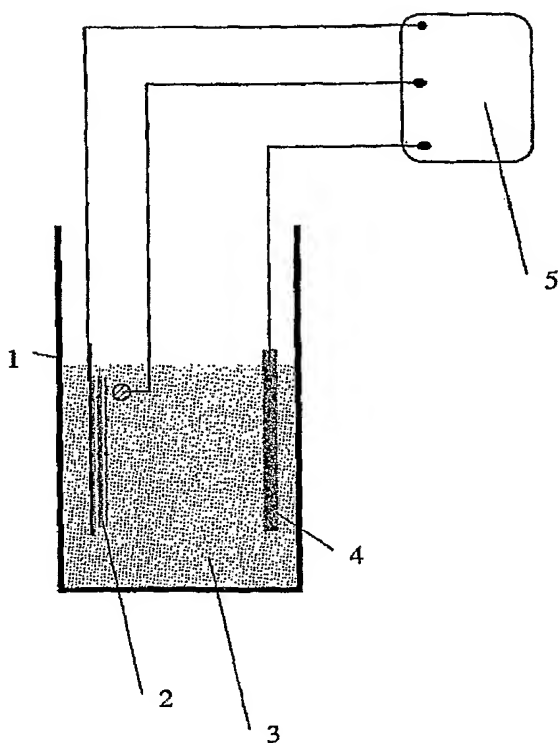
(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO,

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **SKRYABIN, Igor**,
Lvovich [AU/AU]; 76 Schlich Street, Yarralumla, ACT

[Continued on next page]

(54) Title: METHOD FOR ELECTROLYTIC ENGINEERING OF NANO-PARTICULATE LAYERS



(57) Abstract: A method for manufacturing a nano-particulate
electrode for Dye Solar Cells including the steps of providing an
electrically conductive substrate, formation of a nanoparticulate
layer on the substrate., application of dye to the nanoparticulate
layer and an additional step of electrolytic treatment of the
nanoparticulate layer in an electrolyte.

WO 2005/060008 A1



SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *with international search report*

Method for electrolytic engineering of nano-particulate layers

TECHNICAL FIELD

This invention relates to nano-structured materials and
5 their applications; to methods for the production of such
materials. More particularly, this invention relates to
nano-particulate oxide layers formed on a substrate.

10 BACKGROUND TO THE INVENTION

The nanomaterials, in particular- nano-particulate
materials and nano-particulate oxides are used in wide
range of applications: including but not limited to
15 sensors, batteries, capacitors, photovoltaic cell (e.g.
Dye Solar Cells), electrochromic devices, fuel cells and
devices for photocatalytic cleavage and purification of
water.

20 High commercial potential of Dye Solar Cell technology is
achieved through the nano-particulate structure of oxide
layer incorporating designed porosity, that warrants high
surface area, and, thus, - enhanced ability to adsorb
sufficient quantity of dye to effectively capture solar
25 light on the interface between the dye layer and
electrolyte.

It has been recognized that surface properties of nano-
particles are critical for achieving high performance of
30 devices based on nano-particulate materials.

Modifications of the said properties can be performed by
covering each particle by a thin layer of another

-2-

material. The purpose of such coating varies:

- Creating a barrier layer (e.g. junction between two materials with different electronic properties).
5 Benefits of the barrier layer include creation of internal electrical field, that allows for unidirectional transfer of electrons (diode effect).
- Creating a blocking layer (electrical insulation of all or part of the surface of a particle from
10 electrolyte or corrosive material).
- Deposition of materials that absorb in the UV - Visual light - IR spectrum
- Electronic shielding of nano-structured oxides (NSO).
15 Certain materials that reside adjacent to or in the surface of the NSO provide electronic shielding and, thus, prevent undesirable charge transfer through the interface between the surface and an electrolyte. This charge transfer causes leakage current: loss of
20 degradation of a device. Preferably the said Electronic Shielding Materials (ESM) are optically transparent and chemically stable.

Current methods include sol-gel chemistry and several
25 different vacuum deposition techniques. Each technique is limited as each does not allow for fast and precise deposition and achievement of desirable properties of the layers.

-3-

OBJECTIVE OF THE INVENTION

An objective of the present invention is to provide methods for surface modifications of nano-oxides and to
5 improve performance of Dye Solar Cells.

SUMMARY OF THE INVENTION

From one aspect, the present invention provides for
10 formation of complete or incomplete nano-particulate layers on or in the surface of an electrically conductive substrate directly from a colloidal solution by application of negative electrical potential to the substrate and positive electrical potential to a counter
15 electrode. The nano-particles are further interconnected either to materials of the substrate or to each other by either sintering in furnace or by applying an AC electrical field of sufficient magnitude, such as high local current passing between particles resulting in
20 heating of local contact points and fusing the particles together.

From another aspect of the invention, the nano particles are coated by dye. The coating is applied by
25 immersing the electrode into the dye solution and applying an electrical field that promotes movement of charged dye in the solution towards the nano-oxide layer and subsequent bonding of dye molecules to the said nano-oxide particles.

30 In one embodiment in accordance with this aspect of the invention, the application of dye is followed by application of another dye or of another absorber that blocks areas of the nanoparticles that had not been

-4-

covered by the first application of dye. The application of another dye or that of another absorber is conducted in the same manner as that of the first dye, e.g. - from solution and with aid of electrical field, which forces
5 the dye molecules towards the nanomaterial that is normally, but not essentially, a nano-oxide.

According to a further aspect of the invention, a barrier layer is formed on surface of the said
10 nanomaterial. For the purposes of this invention, the surface comprises that region from the interface to a depth of approximately 40 Angstroms or about 10 unit cells. The barrier layer typically comprises metal oxide, electronic properties of which differ from that of
15 original nano-particulate layer. Application of such a barrier layer is conducted in solution by creation of an electrical field that promotes movement of material, in the form of ions, of the barrier layer towards nano-particles with subsequent deposition of this material on
20 surface of the said nano-particles.

In one embodiment in accordance with this aspect of the invention two or more such materials with different electronic properties are deposited.

In a further embodiment in accordance with this
25 aspect of the invention, the substrate is subsequently treated by heat and/or by oxygen to ensure stable bonding of the deposited material to the nano-particles and/or oxidation of the deposited material.

30 From another aspect of the invention an electrolytic treatment is used to modify surface properties of a nanomaterial. In one embodiment a clean and active surface of the nano-particles is achieved by electrolytic

-5-

dissolution of surface material. In another embodiment an electrolytic oxidation ensures carbon free layers of the nano-particulate material.

5 From yet another aspect of the invention the electrolytic deposition as disclosed above is conducted under constant current conditions with imposed voltage limits, such as when voltage reaches a predefined limit (measured with respect to the reference electrode) a control circuitry
10 switches from the constant current to the constant voltage mode, keeping the constant voltage mode until either current drops below a predetermined value or a predetermined amount of electrical charge has passed through the electrolytic solution.

15

It has been found advantageous to perform the said deposition in a series of cycles with progressive increase of charge transferred through the electrolyte solution. Each cycle comprises an insertion and extraction half-
20 cycle. During the insertion half-cycle a material to be deposited is promoted by an electrical field towards the nanomaterial. During the extraction half-cycle the material is removed from the nanomaterial.

Both insertion and extraction half-cycle are performed
25 under current limiting conditions until the voltage reaches a voltage preset magnitude, continuing deposition under voltage limiting conditions until either the deposition current falls to a current preset magnitude or a preset charge has been delivered, and then terminating
30 deposition.

It has been found advantageous to superimpose the constant current/constant voltage insertion/extraction mode with an

-6-

applied AC electrical field. In one example the AC electrical field is applied parallel to the substrate, in another example - perpendicular to the substrate.

5 BRIEF DESCRIPTION OF DRAWINGS

Having broadly portrayed the nature of the present invention, embodiments thereof will now be described by way of example and illustration only. In the following
10 description, reference will be made to the accompanying drawings in which:

Figure 1 is a diagrammatic representation of a set-up for electrolytic treatment of nano-particulate
15 electrode.

Figure 2 demonstrates comparative photovoltaic performance of treated and untreated DSC electrode at 0.3 sun.
20

DETAILED DESCRIPTION OF EXAMPLES

Referring to Fig.1 a working nano-particulate electrode
25 comprises a substrate 1 and a nano-particulate layer of a nanomaterial 2. The working electrode is inserted into an electrolyte 6 in such a way that regions of the nano-particulate layer that are selected for the electrolytic treatment are covered by the solution. A reference
30 electrode 3 is located in close proximity to the nano-particulate layer 1. A counter electrode 4 is opposing the working electrode. Shape and position of the counter electrode are selected to ensure uniform electrical field between the counter and the working electrodes. All the 3

-7-

electrodes are connected to a programmable potentiostat 5.

The following materials are presented in this example:

Working electrode : 12-15 microns thick nano-particulate
5 layer of titanium dioxide (titania) deposited on a
conducting glass substrate (3mm thick Pilkington TEC-15
glass).

The titania layer (approximately 11mm x 8mm) was formed by
10 screen printing of titania paste followed by firing at
maximum of 550 C to achieve good sintering and
interconnection of the titania particles (average particle
size was 12-15nm). The working electrode was prepared
using the standard for Dye Solar Cell technology process,
15 which is available in the prior art.

The electrolytic treatment of the working electrode was
performed as follows:

Reference electrode: Ag/AgCl standard micro-reference
20 electrode.

Counter electrode: Pt wire mesh

Electrolyte: 1.4g of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 10ml of iso-
propanol; 1ml of water was added to the solution.

25 *Electrical characteristics:*

- Current density = 0.1 mA/cm^2 ,
- 5 full cycles with small charging level (5mC/cm^2 in
the insertion half-cycles),
- 30 • 5 full cycles with intermediate charging level
(10mC/cm^2 in the insertion half-cycles),
- 1 insertion half-cycle - charge of 10mC/cm^2 .

- 8 -

Post- treatment:

Following the electrolytic treatment a standard DSC dye was applied to the treated nano-particulate titania and standard cells were constructed. In some cases, the working electrodes were post-fired at various temperatures. Photovoltaic testing at 0.3 sun demonstrated significant improvement in open circuit voltage and fill factor for the treated samples. The maximum efficiency was achieved for the sample, which was post-fired at 250 C (shown in Fig.2).

Referring to Fig. 2 a photovoltaic tests of treated and untreated electrode for DSC demonstrate that the electrolytic treatment results in significant improvement of photovoltaic voltage and power.

20

25

30

- 9 -

Claims:

1. A method for manufacturing a nano-particulate electrode for Dye Solar Cells including the steps of
5 providing an electrically conductive substrate, formation of a nanoparticulate layer on the substrate, application of dye to the nanoparticulate layer and an additional step of electrolytic treatment of the nanoparticulate layer in an
10 electrolyte.
2. A method according to claim 1, wherein the electrolyte contains ions chemically different to the nano-particulate layer and the said electrolytic treatment comprises transfer of material from the
15 electrolyte in the form of ions into the surface of the nano-particulate layer resulting in formation of a barrier layer, electronic properties of which differ from that of the original nano-particulate layer.
- 20 3. A method according to claim 2, wherein the said electrolytic treatment is followed by heating to ensure stable bonding of the barrier layer to the nano-particulate layer.
- 25 4. A method according to claim 1, wherein the said electrolytic treatment comprises partial removal of material from the nanoparticulate layer to the electrolyte.
5. A method according to claim 1, wherein the electrolyte contains ions of UV, visual light and/or
30 Infra red absorbing material.
6. A method according to claim 4, wherein the absorbing material is dye.
7. A method according to any of the preceding claims

- 10 -

wherein the nano-particulate layer comprises a metal or mixed metal oxide.

8. A method according the claim 7, wherein the metal oxide is titanium dioxide.
- 5 9. A method for manufacturing nanoparticulate electrode for DSC including the steps of providing a substrate, electrolytic deposition of the nanoparticulate layer from an electrolyte and application of dye to the nanoparticulate layer.
- 10 10. A method according to any of the preceding claims wherein the electrolytic treatment includes at least one step of transfer of a predetermined amount of electrical charge between the electrolyte and the nanoparticulate layer.
- 15 11. A method according to claim 10, wherein the charge is transferred under constant current conditions with imposed voltage limits, such as when voltage reaches the imposed limit a control circuitry switches from the constant current to the constant voltage mode,
20 keeping the constant voltage mode until either the current drops below a predetermined current value or the predetermined amount of electrical charge has passed between the electrolyte solution and the nanoparticulate electrode.
- 25 12. A method according to claim 10 and claim 11 wherein the electrolytic treatment includes at least 2 subsequent steps (half-cycles), each transferring the predetermined amount of charge; in the first half-cycle the charge is transferred by movement of ions
30 from the electrolyte to the nanoparticulate layer, in the second half-cycle - from the nanoparticulate layer to the electrolyte.
13. A method according to claim 12, wherein the

- 11 -

electrolytic treatment includes at least 2 cycles and predetermined charge in the second cycle is larger than that in the first cycle.

5

10

15

20

25

30

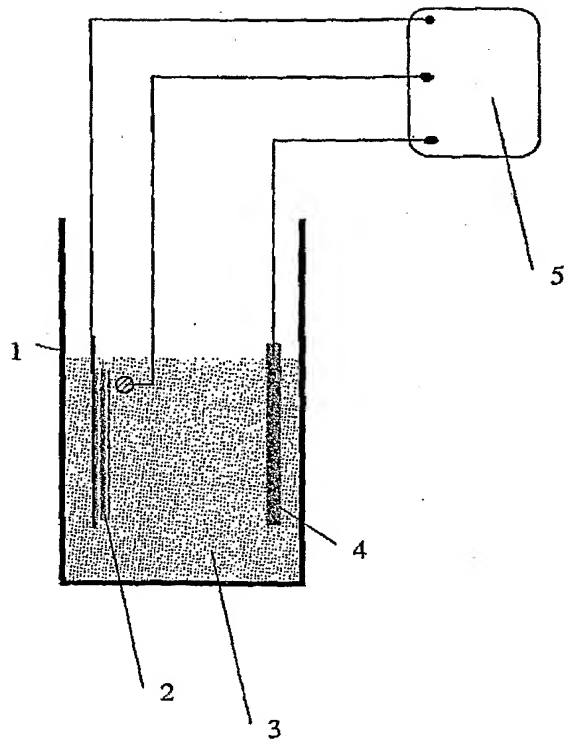


Figure 1.

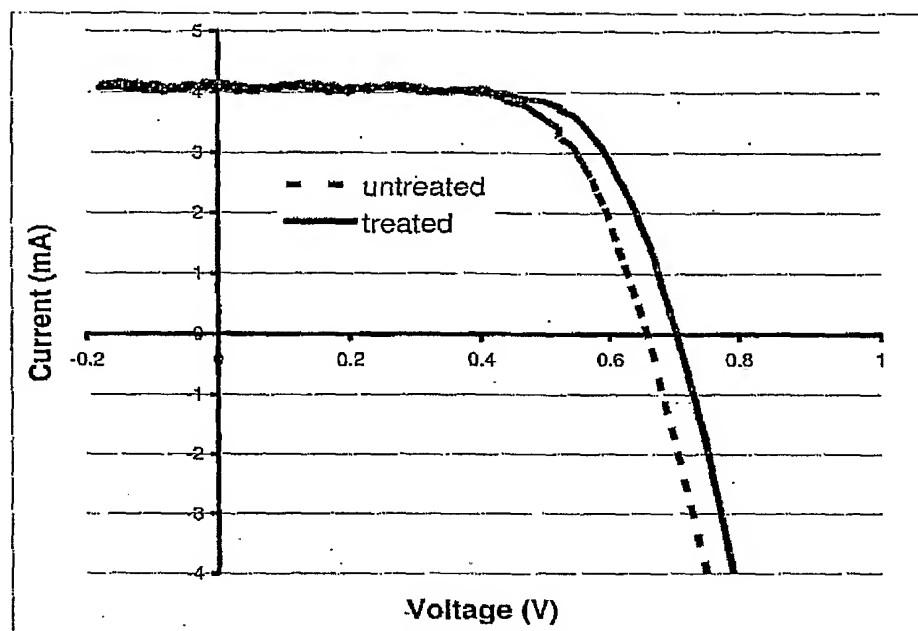


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/001768

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁷ : H01L 31/0224, 31/042 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC ⁷ as above Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Derwent WPI: IPC ⁷ as above and (dye or nano+)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1289028 A1 (Sony International (EU) GmbH) 5 March 2003 Whole Document	
A	EP 1213775 A2 (Seiko Epson Corp) 12 June 2002 Whole Document	
A, P	US 20040067613 A1 (Murofushi et al) 8 April 2004 Whole Document	
<input type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 11 March 2005		Date of mailing of the international search report 16 MAR 2005
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929		Authorized officer DAVID K. BELL Telephone No : (02) 6283 2309

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2004/001768

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
EP	1289028	JP	2003179244	US	2003062082		
EP	1213775	AU	97147/01	CN	1363959	JP	2003163359
		JP	2003163360	US	6683244	US	2002108649
US	2004067613	EP	1363348	WO	02067357		
<p>Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.</p> <p>END OF ANNEX</p>							